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To cite this article: V I Sokolov *et al* 2019 *J. Phys.: Conf. Ser.* **1389** 012078

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## Donor DBH excitons and magnetism of Mn doped ZnO

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**Abstract.** In this paper the results of the study of optical absorption, photo-EPR signals and magnetic measurements of hydrothermal single crystals of zinc oxide doped with manganese were presented. Several lines were detected in optical absorption spectra at the temperature of 4.2 K and 77.3 K for  $\sigma$ - and  $\pi$ - polarizations of light in a 1.72–2.3 eV spectral range. These lines are attributed to a donor exciton  $[(d^5 + h)e]$  that emerges as a result of the Coulomb binding of a free s electron and a hole, which is localized on p–d hybridized states. Properties of these lines are significantly different from the properties of lines of donor and acceptor excitons in II–VI:3d compounds. In EPR-spectra of  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$  crystals the intensity of allowed and forbidden EPR-signals of  $\text{Mn}^{2+}$  ( $d^5$ )-ions does not change under the illumination while the intensity of EPR-signals of unintentional  $\text{Fe}^{3+}$  ( $d^5$ )-ions decreases by 70 %. The value of the magnetic susceptibility of  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$  ( $x = 0.0009$ ) is in linear dependence with temperature, which agrees with the Curie equation. Temperature dependence of the inverse value of the  $\text{Mn}^{2+}$  magnetic susceptibility indicates that the exchange interaction in  $\text{ZnO:Mn}$  crystals is absent. New experimental results allow us to assume that investigated  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$  ( $x = 0.0009$ ) samples are semiconductors in the forbidden gap of which the donor level of  $d^5/d^4$  does not exist. The hybridization of  $d^5$  states of  $\text{Mn}^{2+}$  and  $p$  states of the nearest four oxygen ions  $\text{O}^{2-}$  leads to pushing out the antibonding DBH-states ( $d^5 + p$ ) into the forbidden gap. The transitions of electrons from DBH-states to the conduction band provide a broad band of the impurity absorption in  $\text{ZnO:Mn}$ . Below this band we observed a, b, c and d lines, which are called dbh-donor excitons  $[(d^5+h)e]$ .

### 1. Introduction

Semiconductors II–VI and II–V doped by 3d-elements have been actively studied for a long time in order to understand the crystal energy spectrum role for the modification of the different properties of semiconductors. Many experiments indicate that impurities of 3d metals form energy states of two types in the forbidden gap of semiconductors: Crystal Field Resonance (CFR) and Dangling Bond Hybrid (DBH) states [1, 2]. If a CFR state emerges in the forbidden gap of a semiconductor, then there arise optical transitions with the transfer of an electron from the valence band to a 3d-impurity level or from the 3d-impurity level to the conduction band. The type of charge transfer transition can be



exactly determined by the photo-EPR technique from the weakening of photo-EPR signal of  $d^n$ -configuration or from the arising of photo-EPR signals of  $d^{n+1}$  or  $d^{n-1}$ -configuration [3]. The observation of donor and acceptor excitons below the edge of a charge transfer band provides additional information on the type of the charge transfer [1, 4, 5]. From the systematization of results of 3d-impurities in II-VI semiconductors investigation the universal tendency of 3d-impurity level positions relatively the edges of allowed bands in II-VI semiconductors was obtained [1, 2, 4, 5]. In accordance to this tendency the donor level of  $Mn^{2+}$  ion in II-VI semiconductors is situated in the valence band. If a 3d-impurity creates the CFR-state in the valence band, then an antibonding DBH-state, which is mainly formed by p-states of oxygen ions  $O^{2-}$  with the addition of d-states of  $Mn^{2+}$  ions, is expelled to the forbidden gap as a result of p-d – hybridization.

In theoretical papers the existence of e- and  $t_2$ -states of  $Mn^{2+}$  ions in the forbidden gap of  $Zn_{1-x}Mn_xO$  was predicted [6-8]. In principle the existence of antibonding CFR- or DBH-states, which arise as a result of hybridization of 3d- and 2p-shells of  $(Mn^{2+}-4O^{2-})$ -cluster ( $C_{3v}$ -symmetry) is possible in the forbidden gap. In [9] first results of observation of dbh-donor excitons in  $Zn_{1-x}Mn_xO$  ( $x=0.0009$ ) were presented. In this paper the results of detailed investigations of excitons on the edge of impurity absorption band, allowed and forbidden signals of photo-EPR and magnetic susceptibility of  $Zn_{1-x}Mn_xO$  crystals for exact determination of type of the states in forbidden gap are presented.

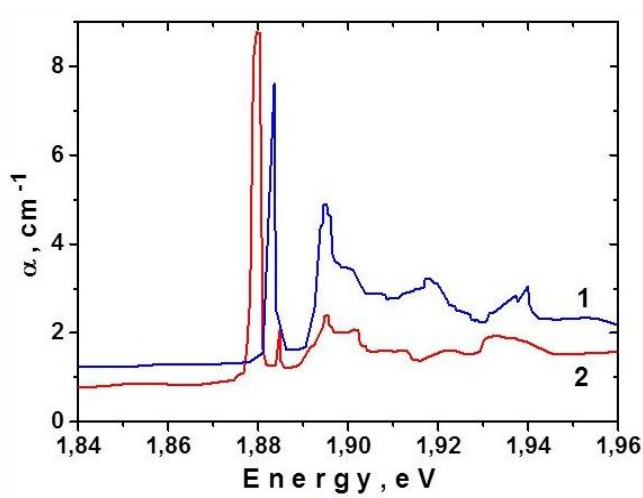
## 2. The details of experiment

The samples for measurements were prepared by the hydrothermal method and had the shape of rectangular parallelepipeds, whose larger face was perpendicular to a crystallographic axis  $C$ . The optical absorption spectra were measured at 77.3 and 4.2 K with the polarized light. The electric field  $E$  of the light wave was perpendicular to the optical axis  $C$  ( $E \perp C$ , i.e.,  $\sigma$  polarization), or parallel to axis  $C$  ( $E \parallel C$ , i.e.,  $\pi$  polarization). The illumination effect on the electronic paramagnetic resonance (photo-EPR) of  $Mn^{2+}$  centers was studied on a EMX Plus Bruker spectrometer at 120 K on a frequency of 9450 MHz. The irradiation was performed through a standard window of a microwave resonator. Light-emitting diodes with the peak wavelengths of 525 nm (2.36 eV) and 464 nm (2.67 eV) and xenonic lamp with light filter were used as the sources. Magnetic measurements were performed on a MPMS-5-XL Quantum Design magnetometer with magnetic field  $H \parallel C$ .

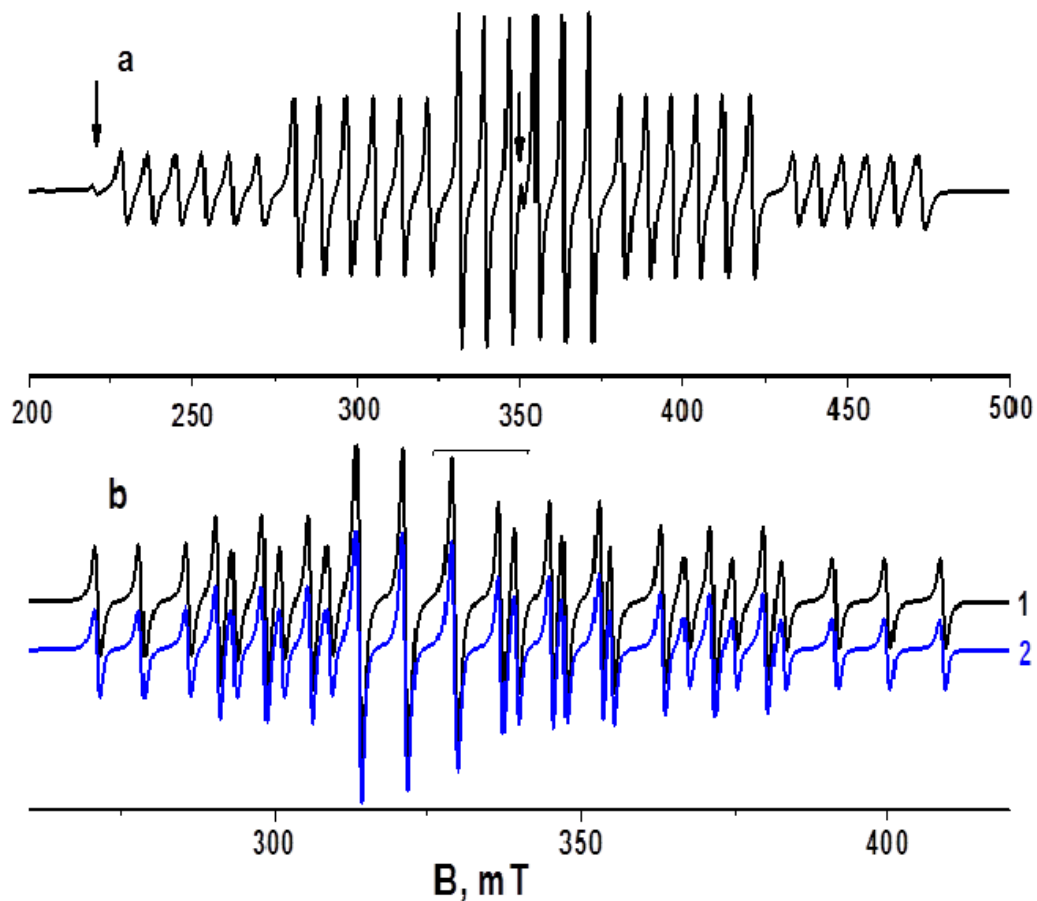
## 3. Results and discussion

Optical absorption spectra of  $Zn_{1-x}Mn_xO$  ( $x=0.0009$ ) single crystals are presented in figure 1. The new lines are spaced away from the visual edge of the broad impurity absorption band by about 200 meV; the intensities of these lines are gradually decreasing with an increase of the energy of the light quantum. In addition to  $a_\pi$ ,  $b_\pi$ ,  $c_\pi$ ,  $d_\pi$ ,  $a_\sigma$ ,  $b_\sigma$ ,  $c_\sigma$ , and  $d_\sigma$  lines, which were observed in [9] for  $x=0.0004$ , in the sample of  $x=0.0009$  new line  $a_\pi$  was observed in the case of  $\pi$ -polarization at the energy very close to the energy of most intensive line  $a_\sigma$  for  $\sigma$ -polarization.

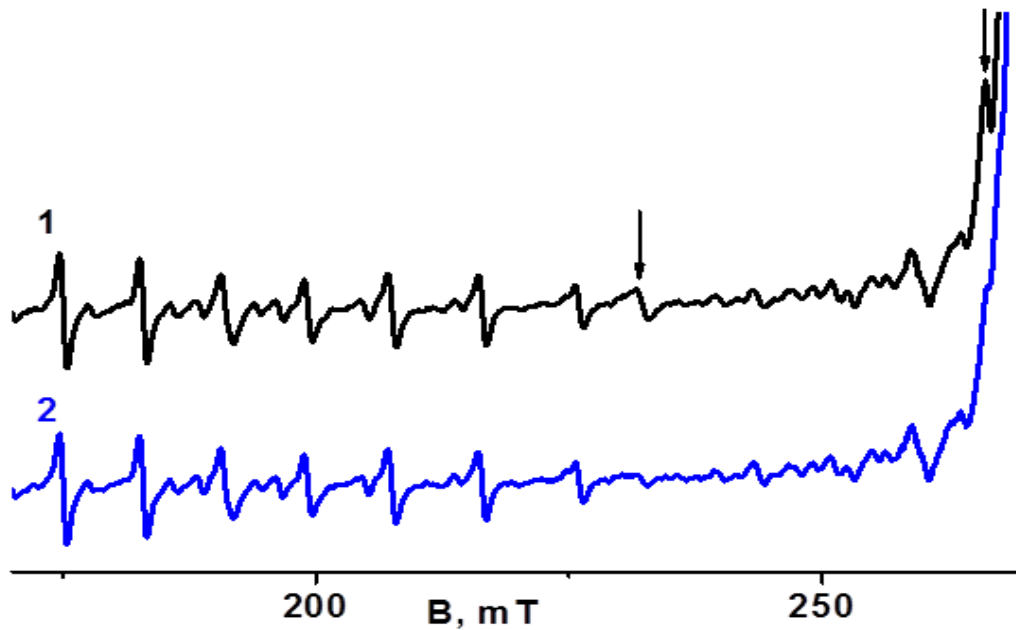
In figure 2a we can see EPR-spectrum of  $Zn_{1-x}Mn_xO$  ( $x=0.0009$ ) single crystal in the dark at  $B \parallel C$ . This spectrum consists of the series of intensive signals. These signals are the evidence of the presence of  $Mn^{2+}$  ions in significant concentration in the crystal [10, 11]. Also we can see two signals from unintentional  $Fe^{3+}$  ions [12-14]. In addition, outside the adducted region of magnetic fields the weak signals, which correspond to  $Fe^{3+}$  centres (which are isolated or associated with  $Li^+$  ions), manifest themselves. In figure 2b we can see EPR-spectrum in the dark at  $B \perp C$ . At this orientation besides the intensive signals (figure 2b) in the region of the weak fields we can see the weak transitions of trigonal centers  $Mn^{2+}$  and isolated centres  $Fe^{3+}$  (figure 3). In perpendicular spectrum the indications of interaction between the  $Mn^{2+}$  ions also are absent.



**Figure 1.** Optical absorption spectra of  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$  ( $x=0.0009$ ) single crystal for  $\sigma$ - (1) and  $\pi$ - (2) polarizations of light at the temperature of 4.2 K.



**Figure 2.** a - EPR-spectrum (derivative of absorption spectrum) of  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$  ( $x=0.0009$ ) single crystal at  $T=300$  K and  $\mathbf{B} \parallel \mathbf{C}$  ( $\mathbf{B}$  - induction of magnetic field). Signals of  $\text{Fe}^{3+}$  centres are marked by arrows,  $\nu=9850$  MHz. b - EPR-spectrum of  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$  ( $x=0.0009$ ) single crystal at  $T=120$  K;  $\mathbf{B} \perp \mathbf{C}$  and  $\nu=9850$  MHz ; 1 – in the dark : 2 – under the illumination by xenonic lamp with light filter.



**Figure 3.** Region of low field of EPR-spectrum of  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$  ( $x=0.0009$ ) single crystal at  $T=120$  K;  $\mathbf{B} \perp \mathbf{C}$ ; 1 – in the dark; 2 - under the illumination by the green light diod. Signals of isolated  $\text{Fe}^{3+}$  ion are marked by arrows

Energy states of isolated  $\text{Mn}^{2+}$  ion, which is situated on the place of  $\text{Zn}^{2+}$  ion in hexagonal ZnO crystal, are described by the trigonal spin Hamiltonian [15]:

$$H_{\text{sp}} = \beta(\mathbf{B}g\mathbf{S}) + (b_{20}O_{20}/3) + ((b_{40}O_{40} + b_{43}O_{43})/60) + (\mathbf{S}\mathbf{A}\mathbf{I}) + (P_{20}O_{20}(\mathbf{I})/3) - g_n\beta_n(\mathbf{B}\mathbf{I}) \quad (1)$$

In (1)  $g$  –  $g$ -factor;  $\beta$  – Bohr magneton;  $O_{nm}$  and  $O_{nm}(\mathbf{I})$  – electronic and nuclear spin operators. The first term in (1) describes the Zeeman interaction. Next two terms describe the splitting without magnetic field due to the interaction with crystal field of cubic or trigonal symmetry. Last three terms correspond to superthin, nuclear quadrupole and nuclear Zeeman interaction.

The ground state of  $\text{Mn}^{2+}$  ions ( $S = 5/2$ ) in magnetic field is splitted into six levels due to the first three terms of (1). Transitions between these six levels cause the thin structure, which consists of five allowed EPR-transitions ( $|\Delta M| = 1$ , where  $M$  is projection of electron spin). Due to the interaction between the electron spin and intrinsic spin of nuclear ( $I = 5/2$ ) the superthin structure is arising; this structure consists of six signals for each transition of thin structure. At  $\mathbf{B} \parallel \mathbf{C}$  EPR-spectrum of  $\text{Mn}^{2+}$  ions consists of 30 intensive allowed (without the changing of  $m$  – projection of nuclear spin) transitions of thin and superthin structures (figure 2a). At  $\mathbf{B} \perp \mathbf{C}$  allowed signals are shifted into the centre of spectrum (due to the decreasing of contribution of spin Hamiltonian second term (1)) and partially overlap one another (figure 2b). In addition, in the region of the low fields weak forbidden transitions of  $\text{Mn}^{2+}$  ions at  $|\Delta M| \geq 2$ ,  $|\Delta m| \neq 0$  and transition of isolated  $\text{Fe}^{3+}$  centres are arising (figure 3). In ZnO unintentional Fe ions, taking place the Zn ions, must be divalent. During the hydrothermal technological process of the production of ZnO the lithium acceptors are arising. This fact promotes the production of  $\text{Fe}^{3+}$  ions, which manifest themselves in EPR- and photoluminescence spectra [13, 16]. We can establish that in our  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$  ( $x=0.0009$ ) single crystal two types of  $d^5$ -configuration – for  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$  ions exist. For the second type of  $d^5$ -configuration thin structure was observed [16].

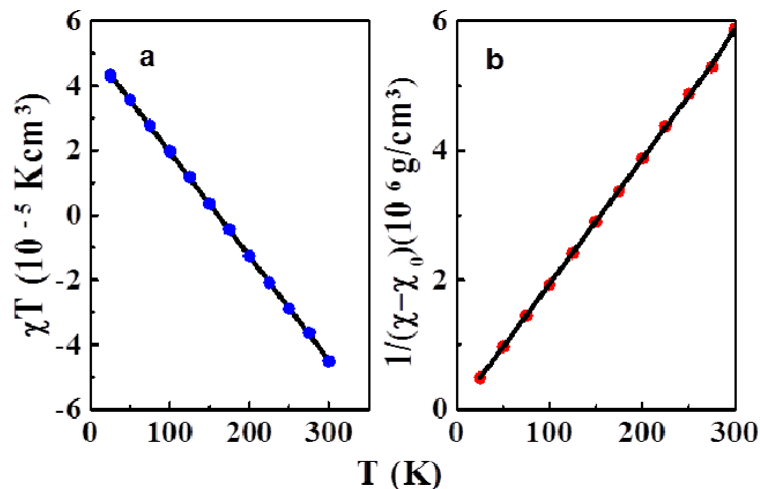
First two peaks of this thin structure are placed in the region of forbidden signals of  $\text{Mn}^{2+}$  centres [12, 13]. This fact facilitates the observation of thin structure signals of  $\text{Fe}^{3+}$  ions at the phone of weak forbidden signals of  $\text{Mn}^{2+}$  ions. It is seen that allowed signals of thin structure of  $\text{Fe}^{3+}$  ions are significantly weaker than forbidden signals of  $\text{Mn}^{2+}$  ions (figure 3) due to low concentration of  $\text{Fe}^{3+}$  ions. The other signals of thin structure of  $\text{Fe}^{3+}$  ions are not manifest themselves at the phone of intensive allowed signals of  $\text{Mn}^{2+}$  ions (figure 2b).

At the illumination of the sample by xenonic lamp with light filter or by light diod we observed the weak changing of intensity of  $\text{Mn}^{2+}$  allowed signals and the changing of frequency of resonator of super high frequency (SHF) (figure 2b). The possible reason of this fact – the changing of concentration of paramagnetic centres.

In the region of weak forbidden signals at  $\mathbf{B} \perp \mathbf{C}$  the illumination of the sample also do not influence the value of signals of  $\text{Mn}^{2+}$  ions, but the intensity of two transition of isolated  $\text{Fe}^{3+}$  ions decreases by 70 % (figure 3). This fact is explained by the possibility of existence of donor ( $\text{Fe}^{3+}/\text{Fe}^{4+}$  or  $d^5/d^4$ ) or acceptor ( $\text{Fe}^{3+}/\text{Fe}^{2+}$  or  $d^5/d^6$ ) levels in the forbidden gap for the  $\text{Fe}^{3+}$  ions, while for  $\text{Mn}^{2+}$  ions the levels with the changing of  $d^5$ -configuration are absent in the forbidden gap. Thus the quota of  $\text{Fe}^{3+}$  ions with  $d^5$ -configuration decreases under the illumination and the value of EPR-signal of these ions sharply decreases.

On figure 4a we can see the values of  $\chi T$  ( $\chi$  – magnetic susceptibility of the crystal). This value is in linear dependence from the temperature  $T$ . This fact points to a good realization of Curie law:

$$\chi = \chi_0 + C/T \quad (2)$$



**Figure 4.** a – Temperature dependence of the multiplication of magnetic susceptibility  $\chi$  and temperature  $T$ . b – Temperature dependence of inverse paramagnetic susceptibility. Round symbols – experimental values; solid lines - approximation

The value of  $\chi_0$  is  $-(3.21 \pm 0.01) \cdot 10^{-7} \text{ cm}^3/\text{g}$ ; the meaning of this value is diamagnetic susceptibility of ZnO matrix. Curie constant  $C$  practically coincides with theoretical value  $5.92\mu_B$  for isolated  $\text{Mn}^{2+}$  ion. In figure 4b we can see the temperature dependence of inverse value of manganese susceptibility  $\chi_{\text{Mn}} = \chi - \chi_0$ . This dependence shows us that the received direct line passes through the point of (0,0). Thus the magnetic data are in good agreement with EPR-data, and we can say that our sample is practically ideal diamagnetic with the isolated  $\text{Mn}^{2+}$  ions.

Let us compare the observed lines in absorption spectrum of  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$  ( $x=0.0009$ ) single crystal with the lines of donor and acceptor excitons in II-VI semiconductors. Earlier donor and acceptor

excitons were observed in II-VI:3d compounds only in electroabsorption spectra [4, 5]. For example in ZnO:Co the zero phonon line in electroabsorption spectra [17] was registered with the intensity of  $3 \times 10^5 \text{ cm}^{-1}$  and repeated with the frequency of LO-phonons of ZnO lattice. Intensive LO-repetitions also were observed for acceptor excitons in ZnO:Ni and ZnO:Cu [4, 18]. In our absorption spectrum of  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$  even most intensive lines  $a_\pi$  and  $a_\sigma$  have not vibrational repetitions. Donor exciton in ZnO:Co and acceptor excitons in ZnO:Ni and ZnO:Cu are observed at the temperature of 4.2 K and not visible at the temperature of 77.3 K. Intensities of our lines  $a_\pi$  and  $a_\sigma$  at the temperature of 4.2 K is near  $8 \text{ cm}^{-1}$ . At the increasing of temperature from 4.2 K to 77.3 K these intensities are decreasing, but the lines remain sufficiently noticeable.

Systematization of many results of investigation of 3d-impurities in II-VI compounds allows us to recognize that donor levels  $d^n/d^{n-1}$  of majority of 3d-impurities are located within the forbidden energy gap. But the donor levels  $d^5/d^4$  of  $\text{Mn}^{2+}$  ion are located in the valence band [1-4, 19, 20] due to significant increasing of third ionization potential of Mn atom in vacuum in comparison of third ionization potentials of Fe and Cr atoms [1, 4, 5]. Donor level  $d^5/d^4$  of  $\text{Fe}^{3+}$  ion must be situated in the valence band analogously to  $\text{Mn}^{2+}$  due to next fact: fourth ionization potentials of Fe is greater than the third ionization potential of Mn at 1.7 times. Because of that we consider that the weakening of EPR-signals of  $\text{Fe}^{3+}$  ions under the illumination by the light at the energy of 2.36 eV takes place due to the changing of the quantity of d-electrons. This changing takes place due to the excitation of electron transitions to acceptor level  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ( $d^5/d^6$ ). This level is located at the lesser distance from the top of the valence band in comparison to the illumination energy. Earlier there was no information about the existence of charge transfer levels of  $\text{Fe}^{3+}$  ions in the forbidden gap of ZnO. The significant difference between the a, b, c and d lines in  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$  ( $x=0.0009$ ) absorption spectrum and lines of donor exciton in ZnO:Co electroabsorption spectrum and the different changes of EPR-signals for  $d^5$ -configurations of  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$  ions under the illumination allow us to conclude that donor  $d^5/d^4$  and acceptor  $d^5/d^6$  levels of  $\text{Mn}^{2+}$  ions do not exist in the forbidden gap of zinc oxide. Antibonding DBH-states are expelled into the forbidden gap. These states arise as a result of hybridization between 3d-orbitals of  $\text{Mn}^{2+}$  ions and dangling p-bonds of four nearest  $\text{O}^{2-}$  ions in  $(\text{Mn}^{2+} + 4\text{O}^{2-})$  cluster with  $C_{3v}$ -symmetry.

#### 4. Conclusions

It was shown that intensities of lines in absorption spectrum of  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$  ( $x=0.0009$ ) single crystal increase with the increasing of Mn concentration and are weakened with the increasing of temperature from 4.2 K to 77.3 K. In  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$  ( $x=0.0009$ ) single crystal photo EPR-signals of  $\text{Mn}^{2+}$ -transitions do not change under the illumination by the light at the energy in the region of impurity absorption, while EPR-signals of  $\text{Fe}^{3+}$  unintentional ions are weakened by 70 % under the illumination. These new experimental results allow us to conclude that impurity absorption in  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$  crystals is called out by transitions from antibonding DBH-states to the bottom of conduction band. It is also shown, that  $\text{Fe}^{3+}$  ( $d^5$ ) ion has the acceptor level ( $d^5/d^6$ ) in the forbidden gap of zinc oxide.

#### Acknowledgements

The authors are grateful to V.I. Anisimov and A.V. Lukoyanov for the discussion of results.

The research was carried out within the state assignment of Minobrnauki of Russia (theme "Magnet" No.AAAA-A18-118020290129-5, theme "Electron" No. AAAA-A18-118020190098-5) and within the state assignment no. 3.6115.2017/8.9 of the Ministry of Education and Science of the Russian Federation for the Ural Federal University, with the support of the grant of Ural branch of Russian Academy of Science № 18-10-2-6.

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